

Appl. No. 09/945,393

REMARKS

Claims 1-8, 10-13, 15-33, 35-40, and 42-50 are pending in the application with claims 1, 5, 8, 10, 11, 13, 15, 20, 25, 28, 29, 30, 35, 36, 38, 39, 42, 45, and 50 amended herein and claims 9, 14, 34, and 41 canceled herein.

Claims 1-13, 15-19, 36-41, 43, and 44 stand rejected under 35 U.S.C. 102(e) as being anticipated by Raaijmakers. Claims 14, 20-35, 42, and 45-50 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Raaijmakers. Applicant requests reconsideration.

Amended claim 1 sets forth a dielectric material forming method that includes, among other features, forming a second monolayer on a first monolayer, one of the first and second monolayers containing tantalum and oxygen and the other of the first and second monolayers containing oxygen and zirconium. The method includes forming a dielectric layer containing the first and second monolayers, the dielectric layer exhibiting a dielectric constant greater than the first monolayer. Pages 2-3 of the Office Action allege that Raaijmakers discloses each and every limitation of claim 1. However, review of Raaijmakers reveals that it does not disclose forming a first monolayer containing tantalum and oxygen and forming a second monolayer containing zirconium and oxygen and forming a dielectric layer containing the first and second monolayers.

Applicant acknowledges a discussion in paragraph [0041] of Raaijmakers regarding a variety of dielectric materials including ZrO_2 . However, paragraph [0041] does not disclose a dielectric layer containing tantalum, zirconium, and oxygen. Applicant also acknowledges a discussion in paragraph [0113] to [0122] regarding many dielectric layers including first metal/oxygen/second metal/oxygen complex metal oxides in paragraph [0115] and TiO_2 mixed with Ta_2O_5 in paragraph [0117].

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How ever, Raaijmakers does not disclose a dielectric layer containing tantalum, zirconium, and oxygen, as set forth in claim 1. Anticipation requires disclosure of each and every limitation, accordingly, Raaijmakers does not anticipate claim 1. Claims 2-7 depend from claim 1 and are not anticipated at least for such reason as well as for the additional limitations of such claims.

Amended claim 8 sets forth a dielectric material forming method that includes, among other features, chemisorbing a second dielectric material on a first dielectric material, one of the first and second materials containing oxygen, titanium, and zirconium. The method includes forming an enhanced dielectric material containing the first and second materials, the enhanced dielectric material exhibiting a dielectric constant greater than the first material. Review of Raaijmakers, in particular the paragraphs cited above, does not reveal disclosure of a dielectric material containing oxygen, titanium, and zirconium. Accordingly, Raaijmakers fails to disclose each and every limitation of claim 8 and does not anticipate claim 8. Claims 10-13 and 15-19 depend from claim 8 and are not anticipated at least for such reason as well as for the additional limitations of such claims not disclosed. For example, amended claim 13 sets forth that the first material contains tantalum and oxygen. Raaijmakers does not disclose a dielectric material forming method that produces an enhanced dielectric material containing oxygen, titanium, zirconium, and tantalum, as set forth in claim 13.

As may be appreciated from the discussion above regarding the deficiencies of Raaijmakers as applied to claims 1 and 8, claims 20-33, 35-40, and 42-50 are not anticipated by Raaijmakers. Applicant further asserts that Raaijmakers does not suggest dielectric material containing oxygen, tantalum, and zirconium or dielectric

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material containing oxygen, tantalum, titanium, and zirconium. At least for such reason, the pending claims discussed above are patentable over Raaijmakers.


Applicant herein establishes adequate reasons supporting patentability of claims 1-8, 10-13, 15-33, 34-40, and 42-50 and requests allowance of all pending claims in the next Office Action.

A Form PTO-1449 returned to the Applicant indicates that a copy was not provided for Reference AS listed under Other References. Applicant's records indicate that a copy was provided with the IDS accompanied by the subject Form PTO-1449. A clean copy of the previous Form PTO-1449 and the cited reference is included herewith. Applicant requests initialing of Reference AS and return of a copy of the initialed Form PTO-1449.

Respectfully submitted,

Dated: 03 Dec 2003

By:


James E. Lake
Reg. No. 44,854

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U.S. PATENT DOCUMENTS							
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OTHER REFERENCES (including Author, Title, Date, Pertinent Pages, Etc.)							
	AR		R.F. Cava, W.F. Peck Jr., & J.J. Krajewski, "Enhancement of the dielectric constant of Ta ₂ O ₅ through substitution with TiO ₂ ", Nature, Vol 377, September 21, 1995, pages 215-217				
	AS		J.Y. Gan, Y.C. Chang, and T.B. Wu, "Dielectric property of (TiO ₂) _x -(Ta ₂ O ₅) _{1-x} thin films", Applied Phys. Letters 72 (3), January 19, 1998, pages 332-334				
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Dielectric property of $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ thin film.

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$(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ thin films were prepared with radio-frequency magnetron sputtering deposition in this study. The dielectric constant measured from these films appears to critically depend on the amount of TiO_2 incorporated into the film and post-anneal condition. The composition dependence was found similar to that reported on $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ bulk. The highest value of dielectric constant is about 55 for a TiO_2 content of 8% and annealing at 800°C . Compared to pure Ta_2O_5 thin films, significant enhancement in dielectric constant is obtained by adding small quantity of TiO_2 . © 1998 American Institute of Physics. [S0003-6951(97)02841-6]

Recently, Cava *et al.*¹ have reported that the dielectric constant of tantalum oxide (Ta_2O_5) can increase from 35.4 to 126.2 by adding about 8 mol % of titanium oxide (TiO_2). Ta_2O_5 has been studied intensively as the dielectric for the next generation high density electronic memories because of its higher dielectric constant as compared with the oxide/nitride/oxide stack currently used.²⁻⁷ In addition, both TiO_2 and Ta_2O_5 films can be fabricated with chemical vapor deposition (CVD) which is a common technique used in the current integrated circuit (IC) fabrication.⁸ In consequence, their results appear to be very attractive since further improvement on the dielectric constant would extend Ta_2O_5 application in electronic memory to even higher density.

Their measurements were carried out on the $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ bulks that were prepared with a standard ceramic processing technique. The processing temperature is 1400°C ; that is well above the allowed temperature for current IC processing. As a result, it is important to examine if the same properties can be reproduced from thin $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ film that are fabricated at lower temperature.

In this letter, we show that similar composition dependence of dielectric constant is observed in thin $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ films. Significant increase of dielectric constant is also found when the films are crystallized during post-anneal. Nevertheless, the highest dielectric constant measured in this work is about 55; that is much less than the value reported on bulks.

Figure 1 is the schematic drawing of the capacitor fabricated in this study. The substrate was a thermally oxidized Si wafer deposited with Pt ($\sim 1500 \text{ \AA}$) that serves as a bottom electrode. $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ films were deposited with an rf magnetron sputtering system. Targets used in the deposition were made with various compositions of Ta_2O_5 and TiO_2 powders that were mixed homogeneously and fired at 1000°C for 2 h. The deposition was carried out at 200°C and in the oxygen-containing ambient to suppress oxygen deficiency of the deposited films as much as possible. Film thickness was kept around 1100 \AA of which the exact value depends on the film composition. The composition of targets and films were examined primarily with energy dispersive spectrometer (EDS) of which accuracy has been calibrated against wavelength dispersive spectrometer (WDS). Capacitance

measured with HP 4284A was carried out at zero bias and 1 MHz.

Figure 2 shows the film composition as the function of target's, both are expressed in mole fraction of TiO_2 . From the result of linear fit, the line in the figure, it appears that composition of films's and target's is pretty close to each other, the slope of fit is 1.00 ± 0.03 . The larger deviation found in the high TiO_2 fraction case is not clear, possibly caused by competing incorporation between Ti and Ta during deposition. The fit also helps in determining the composition of film prepared from the target with a 1% TiO_2 addition since it is hardly detectable in EDS and WDS. Film's composition is summarized in Table I with other results.

Figure 3 is the dielectric constant plotted with the mole fraction of TiO_2 . The typical film thickness of $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ is around 1100 \AA . Two sets of results are shown in the figure; one is measured from the as-deposited films, the other is obtained from the films being annealed at 800°C for 1 h in N_2 ambient. In either case, the dielectric constant strongly depends on the amount of TiO_2 . It first increases with the addition of TiO_2 , then drops sharply as the fraction of TiO_2 continues to increase. The highest dielectric constant in both cases appears at the same fraction of TiO_2 ; i.e., around 8% of incorporation. This is in agreement with what was observed in bulk $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$. It is also noted that high-temperature anneal seems to enhance the dielectric constant for all compositions. For example, the dielectric constant of

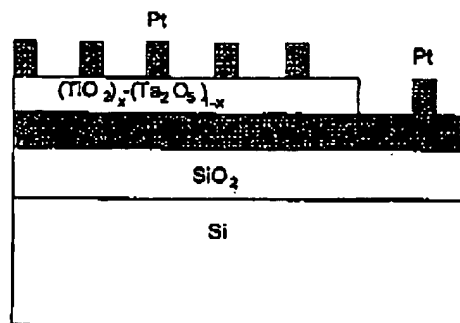


FIG. 1. The schematic drawing of $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ capacitors.

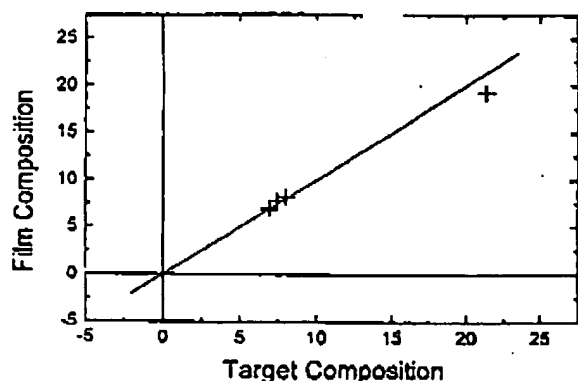


FIG. 2. Film composition as a function of target composition. Both axes are expressed in mole fraction of TiO_2 .

$(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$ films has increased from 30 to 55 after an 800 °C anneal.

The crystalline phases of all films have been examined with a conventional x-ray diffractometer. Figure 4 is the result of x-ray diffraction of $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$ films that were annealed under various conditions. The films under examination are of the same thickness (1100 Å) and were being deposited on the same bottom Pt electrode. Except for the as-deposited films, all were heat treated for 1 h under the specified temperature. Apparently, the film remains amorphous for the annealing temperature below 600 °C. For temperature higher than 800 °C, the crystalline structure starts to form and was identified to be the metastable H' monoclinic phase which is believed to be the same phase observes on bulk $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$.

It is found that the dielectric constant critically depends on whether the crystalline phase has formed. Figure 5 is the dielectric constant of $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$ films plotted as the function of annealing temperature. The film thickness was measured to be 1100 Å, and the capacitance measurement was still carried out under zero bias and at 1 MHz. As shown in the figure, the dielectric constant remains low and unchanged for the as-deposited and 600 °C annealed films. However, the dielectric constant shoots up as the annealing temperature is over 800 °C which is exactly the crystallization temperature being detected from x-ray diffraction. Once the crystalline phase has appeared, the dielectric constant is again relatively independent of the annealing temperature.

Table I lists the dielectric constant from bulk¹ and film (annealed at 800 °C) of the same composition. Note that some of bulk results were obtained with interpolation which may not be exact but would not be too far off either. Evidently, the dielectric constant measured from films is significantly less than that of bulk's except for the case for 1%

TABLE I. The dielectric constant of $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ bulks and films.

$x =$	0.01	0.07	0.08	0.082	0.193
film ^a	40.6	50.9	54.7	45.1	33.4
bulk ^b	27.8	108.5	126.2	123.6	60.8
film/bulk ratio	1.46	0.47	0.43	0.36	0.55

^aAnnealed at 800 °C.

^bInterpolated from Ref. 1.

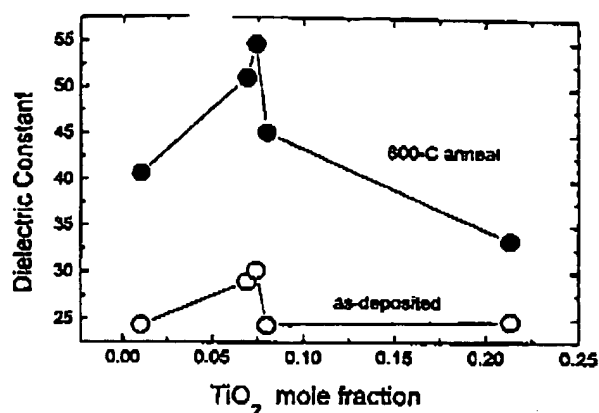


FIG. 3. Dielectric constant as a function of TiO_2 incorporation. The measurement was performed at zero bias and 1 MHz with dielectric film thickness around 1100 Å.

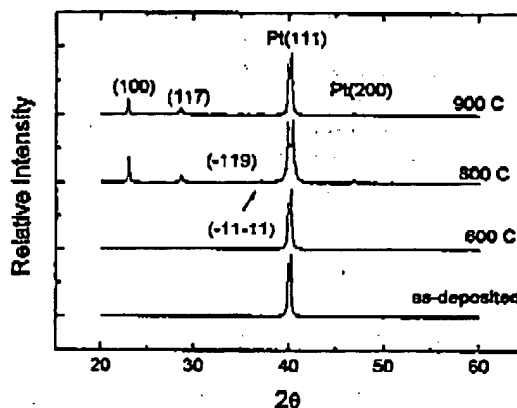


FIG. 4. X-ray diffraction of $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$ films (1100 Å) annealed under various conditions.

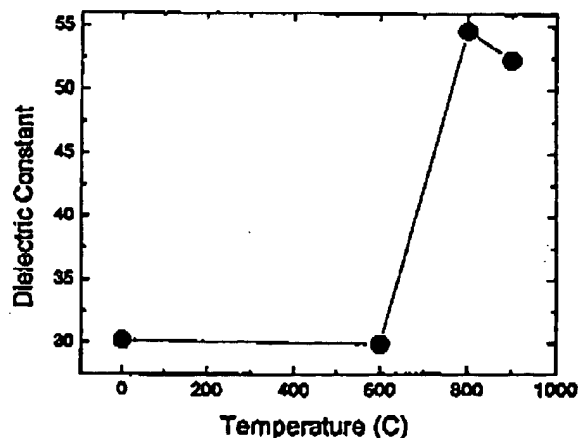


FIG. 5. Dielectric constant of $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$ films as a function of annealing temperature. The measurement was performed at zero bias and 1 MHz. The film thickness is 1100 Å.

incorporation. Since the composition is roughly the same for both film and bulk, it is then obvious that the heat treatment may play an important role in determining the dielectric constant. From the dielectric constant ratio of film to bulk, which is not a constant, the effect of heat treatment is composition dependent too.

To summarize, we have shown that the dielectric constant of Ta_2O_5 thin film, like its bulk form, can also be greatly enhanced by adding a small quantity of TiO_2 . Such an enhancement critically depends on the amount of TiO_2 incorporated, and also appears on both crystalline and amorphous structures. As compared to the bulk value, the highest dielectric constant of the crystallized film is much smaller. The exact mechanism responsible for the enhancement is yet to be found.

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